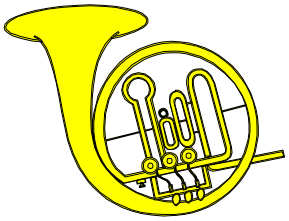
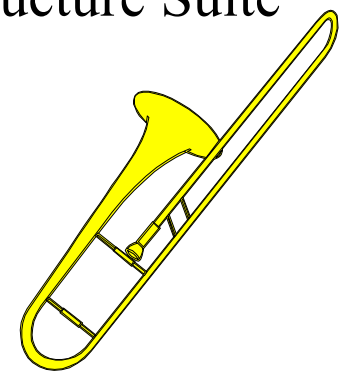
BRASS

The Bremen Rietveld Analysis and Structure Suite



Version 1.0 β

User Manual



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1 Preface and *BRASS* essentials

Finally, the first version of *BRASS*, the *Bremen Rietveld Analysis and Structure Suite*, has been released. *BRASS* is a non-commercial program[1]. However, its development has been sponsored partially by a grant from Panalytical (Almelo, The Netherlands) who also gave permission to use some modules of the old PC-Rietveld plus program (see below for further details).

BRASS is designed to perform quantitative, qualitative and structural phase analyses based on powder diffraction data and crystallographic structure models. It is the main target of *BRASS* to provide a common platform for tasks which are often designated stand-alone programs. This is especially true for the Rietveld analysis along with the display and manipulation of structural models.

The program package *BRASS* can be downloaded from the home page (www.zekam.uni-bremen.de) of the crystallography group at university of Bremen. It should be noted that the program has been developed for our internal use and therefore its usage at external sites will not be supported. However, any useful hints and relevant information on bugs and any suggestions for improvements will be appreciated. We shall put a bug report on our home page as well as the latest information on program modifications.

The release of *BRASS* was delayed several times in order to make the program more robust and stable running for external users who do not know how to get around the numerous pitfalls. The set-up of the current short description for the program handling of *BRASS* was responsible for the latest delay – we simply forgot to write it earlier... It is now included in the program package as a preliminary users manual. It will be extended extensively in the near future (whatever "near" means in this context). As usual, about 90% of programming time is consumed for the last 10% of finishing, debugging, and documenting the program. So we are sending our apologies to all those who are waiting already for a long long time that *BRASS* becomes available.

The program package *BRASS* consists of several modules, most of them programmed in Delphi except the Rietveld kernel and the Fourier calculations which are written in FORTRAN. More than 50% of the code is completely rewritten or programmed from scratch, the rest is based on extensively modified codes of earlier versions. It should be noted that all

[1] It is free of charge for all interested users but it must not be resold to third parties.

those authors who wrote some initial codes or contributed to some modules of the programs deserve a big share of the credit attributed to *BRASS*.

The Rietveld method was introduced by RIETVELD (1967a, 1969) originally written in ALGOL (RIETVELD 1967b). The program kernel used in *BRASS* can be considered a derivative of the FORTRAN program written by WILES AND YOUNG (1981), and extensively modified by HILL AND HOWARD (1986), and FISCHER ET AL. (1993) who programmed the PC-Rietveld plus package distributed by the X-ray equipment supplier Philips Analytical (Almelo) which is now Panalytical. The company granted permission to use the codes for a freeware version and sponsored the developments. The well established code has been modified again and extended extensively (BIRKENSTOCK, FISCHER AND MESSNER, 2003).

The latest developments are: At first a reformulation of the traditional Pseudo-Voigt profile function according to THOMPSON, COX AND HASTINGS (1987) in order to be able to separate instrumental and sample contributions to the profile. Secondly the consideration of anisotropic sample effects using the Pseudo-Voigt function, i.e. anisotropic strain according to STEPHENS (1999) and a simple model for the description of anisotropic average crystallite dimensions.

Another version of the program kernel described by FISCHER, MESSNER AND KASSNER (2000) with extensions written by Dethard Kassner (Glashütten-Oberems) is not yet released and distributed. The numerical part of the FOURIER program is based on Allan Zalkin's FORDAP Fourier program [Lawrence Berkeley Laboratory, Berkeley, CA] in its version modified by James A. Ibers [Northwestern University, Evanston, IL]. The current version including the 2D and 3D graphics for the representation of the Fourier maps has been written by MESSNER AND FISCHER (2003). *STRUPLO*, initially programmed in FORTRAN by Fischer (1985) is completely rewritten (FISCHER AND MESSNER, 2003) in Delphi with extensive modifications. The program uses the BURZLAFF AND HOUNTAS (1982) routine for the derivation of the symmetry operators from the Hermann-Mauguin space group symbol translated to Delphi.

BIRKENSTOCK, J., FISCHER, R.X., MESSNER, T. (2003): *BRASS* 2003: *The Bremen Rietveld Analysis and Structure Suite*. Zentrallabor für Kristallographie und Angewandte Materialwissenschaften, Fachbereich Geowissenschaften, University of Bremen

BURZLAFF, H., HOUNTAS, A. (1982): *Computer program for the derivation of symmetry operations from the space-group symbols*. J. Appl. Crystallogr. **15**, 464-467.

FISCHER, R.X. (1985).: *STRUPLO84, a Fortran plot program for crystal structure illustrations in polyhedral representation*. J. Appl. Crystallogr. **18**, 258-262.

FISCHER, R.X., MESSNER, T. (2003): *STRUPLO 2003*. Zentrallabor für Kristallographie und Angewandte Materialwissenschaften, Fachbereich Geowissenschaften, University of Bremen.

FISCHER, R.X., MESSNER, T., KASSNER, D. (2000): *BRASS: The Bremen Rietveld Analysis and Structure Suite*. Berichte aus Arbeitskreisen der DGK Nr. 9. VII. Workshop Powder Diffraction. Structure Determination and Refinement from Powder Diffraction Data. Ed. R.E. Dinnebier, Deutsche Gesellschaft für Kristallographie (2000) 201 - 208.

FISCHER, R.X., LENGAUER, C., TILLMANNS, E., ENSINK, R.J., REISS, C.A., FANTNER, E.J. (1993): *PC-Rietveld plus, a comprehensive Rietveld analysis package for PC*. Materials Science Forum **133-136** (1993) 287-292.

HILL, R.J., HOWARD, C.J. (1986): *A computer program for Rietveld analysis of fixed wavelength X-ray and neutron powder diffraction patterns*. Australian Atomic Energy Commission Research Establishment, Research Report M112 (1986).

MESSNER, T., FISCHER, R.X. (2003): *Graphical representation of Fourier maps and grid search analyses*. Zentrallabor für Kristallographie und Angewandte Materialwissenschaften, Fachbereich Geowissenschaften, University of Bremen.

RIETVELD, H.M. (1967a): *Line profiles of neutron powder-diffraction peaks for structure refinement*. Acta Crystallogr. **22**, 151-152.

RIETVELD, H.M. (1967b): *An ALGOL program for the refinement of nuclear and magnetic structures by the profile method*. Reactor Centrum Nederland, Research Report 1967.

RIETVELD, H.M. (1969): *A profile refinement method for nuclear and magnetic structures*. J. Appl. Crystallogr. **2**, 65.

WILES, D.B., YOUNG, R.A. (1981): *A new computer program for Rietveld analysis of X-ray powder diffraction patterns*. J. Appl. Crystallogr. **14**, 149-151.

January 12, 2004

The *BRASS* band
at University of Bremen

2 Implementation

1. Download SETUP*BRASS*.EXE from our primary internet site at www.zekam.uni-bremen.de
2. Run the file SETUP*BRASS*.EXE and follow the instructions given during the setup dialog.

3 General organization of *BRASS*

On startup of *BRASS* you see the screen given in Fig. 3-1. The general organization is indicated by the displayed description boxes. Note: You can perform any action while the *start-up information window* is visible for a few seconds.

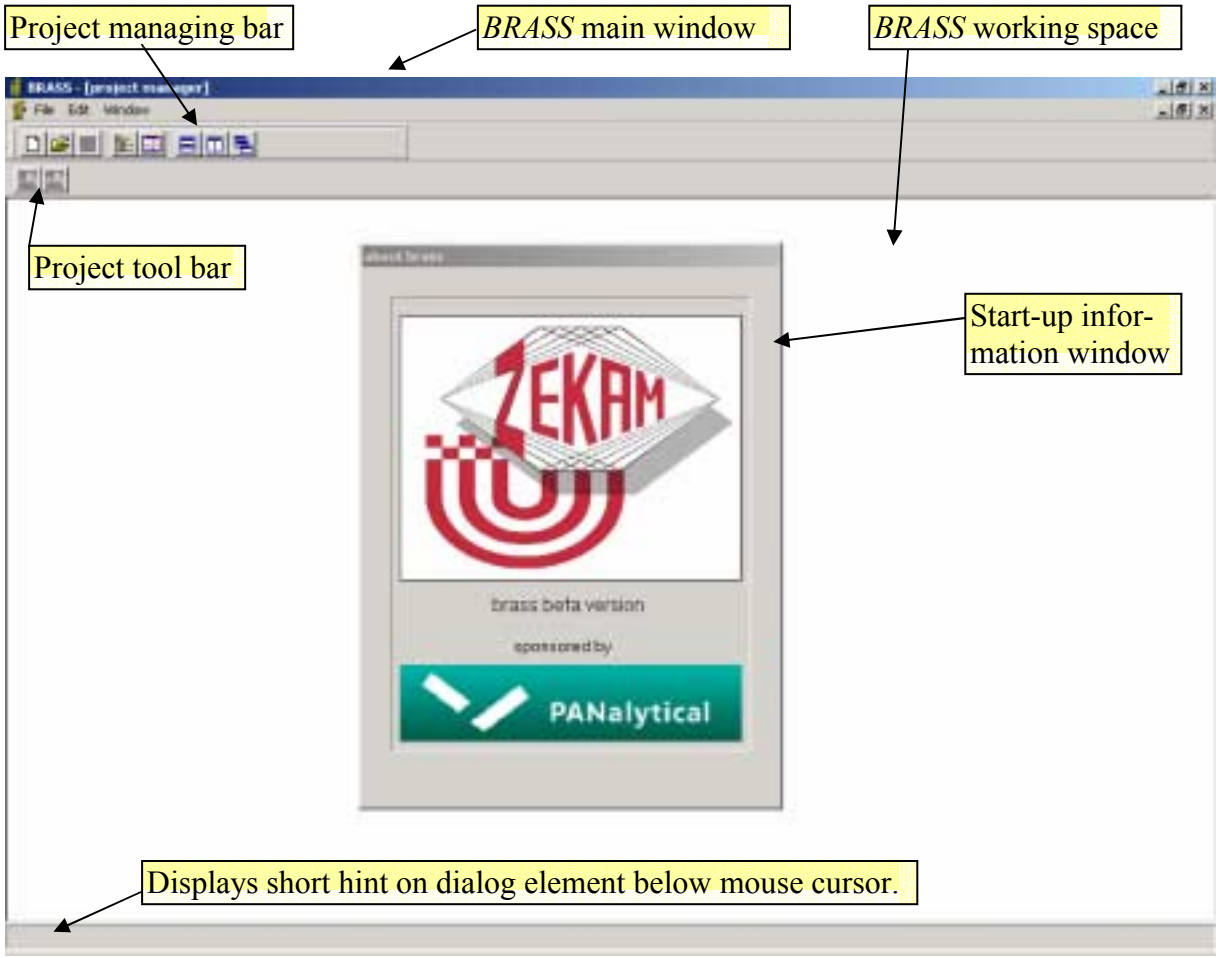


Fig. 3-1: *BRASS* main window after program start-up.

From the menu you can start all available actions. The commands from the menus *file*, *job* and *window* are accessible by specidfied buttons of the *project managing bar*. The *BRASS* working space contains one or more job windows: The job window *project manager* is always

visible and you cannot close it. The job windows *rietveld*, *rietveld plot viewer*, *STRUPLO* and *fourier* are only displayed if the respective job has been started by either a *job* command or one of the buttons in the project managing bar. These latter windows may be closed and re-opened at any time.

A *STRUPLO* or a *rietveld plot viewer* job can be started any time without having opened or created a *BRASS* project in advance. I.e. you can simply run a *STRUPLO* or a *rietveld plot viewer* job right after the startup of *BRASS*. Performing a *rietveld* or a *fourier* job is only feasible after you have created or opened a *BRASS* project.

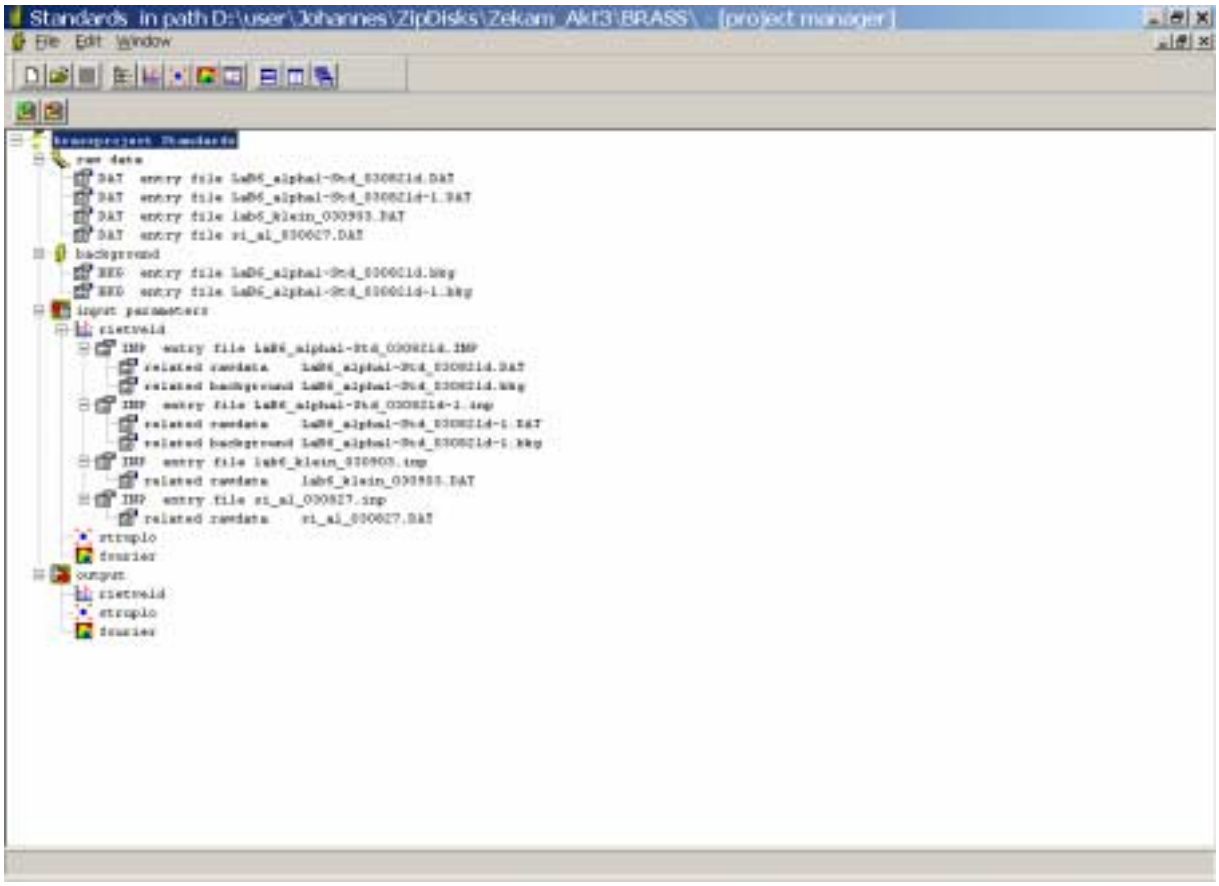


Fig. 3-2: The *project manager* of *BRASS*. You can assemble as many *rietveld*, *STRUPLO* and *fourier* jobs in your *BRASS* project as you wish. Simply run the related module by a double click on the respective file in the list.

BRASS provides the *project manager* (see Fig. 3-2) as its central managing unit. All types of files supported by *BRASS* are registered in the *BRASS* project here and are automatically assigned to the respective folders which are displayed in an *Explorer*-like tree view. The predefined main folders are *raw data*, *background*, *input parameters* and *output*. *Raw data* contains all registered raw data files in the Rietveld DAT format. *Background* lists all registered files which are generated during a Rietveld job when the background subtraction is performed by hand.

Input parameters has subfolders for *rietveld*, *STRUPLO* and *fourier*. All input files are managed here. Furthermore, for a *rietveld* job it is shown, which raw data and background files are associated with an input file, if so defined by the user. This feature allows using the same raw data and/ or background file for different Rietveld jobs, e.g. to compare the impact of different input models or different refinement strategies on the respective results.

Output is subdivided into the same subfolders as *input parameters*. Currently there is no need to register any output files though, since in this version no viewers are linked to the various types of output files. This is an option for future developments.

4 Quick guide

4.1 Creating/ Opening a project and using the project manager

After the startup of *BRASS* you may either create a new *BRASS* project or open a supported file, i.e. a *BRASS* project file *.BPR, a *STRUPLO* input *.BST, a Rietveld plot file *.PLT or a Fourier file *.(Akt hier weiter: Thomas nach Dateiendung/en fragen.)

To **create a new project** simply choose *New* from the *file* menu or press the button *new* in the project managing bar. By pushing *create* in the following dialog *create new project* the project manager displays the predefined *BRASS* project structure.

Alternatively you can **open an existing *BRASS* project** (file type *.BPR) by selecting *open* from the *file* menu or by pushing the button *open* in the *project managing bar*. You can also open an existing *BRASS* project by a double click on a *.BPR file in your *Windows Explorer*.

Now you can proceed by either running one of the *BRASS* jobs where you can open the respective single files or by directly **adding supported files to the project**. For the latter click on in the *project tool bar*. Now you can choose any supported file from a common Windows open dialog. When e.g. choosing a *.DAT file *BRASS* assigns it to the folder *raw-data* and then asks you to open background data and an input file if you have any. If you want to **remove a specific entry from your project** just select the entry in your project tree and then push the button in the *project tool bar*. Note: This action does not delete the selected file from your hard disk.

In order to **run a *BRASS* job** which is related to a specific file in your project simply perform a double click on the respective entry in your project tree. E.g. a double click on a *.INP file entry automatically opens the Rietveld window, a double click on a *.BST file entry invokes the *STRUPLO* window.

4.2 Running a Rietveld job

4.2.1 Using an existing Rietveld input file

Follow the instructions "**adding supported files to the project**" in 4.1 in order to add an existing *.INP file to your current project. In the following dialog you are asked to open related *.DAT and *.BKG files if you wish to do so.

Note: It is not recommended to open the Rietveld window first and open an INP file from within the Rietveld window though this option is still available in this version.

4.2.2 Creating a new Rietveld input file

To create a new Rietveld INP file open the Rietveld window from the *job* menu or by pushing the respective button in the *BRASS managing bar*. Then push the modules' *new inp* button to display the related dialog where you have to type in a new name for the *.INP file. After that you may select a raw data file (type *.DAT) and a *.BKG file to be related to the newly created *.INP file. If you do not choose a *.DAT file, you can only run the Rietveld calculation in simulation mode, i.e. the refinement of parameters is disabled.

4.2.3 Preparing a Rietveld run

The main page *model and report* of the Rietveld module supplies all necessary dialog elements to define the Rietveld input model of which selected parameters are to be refined. To

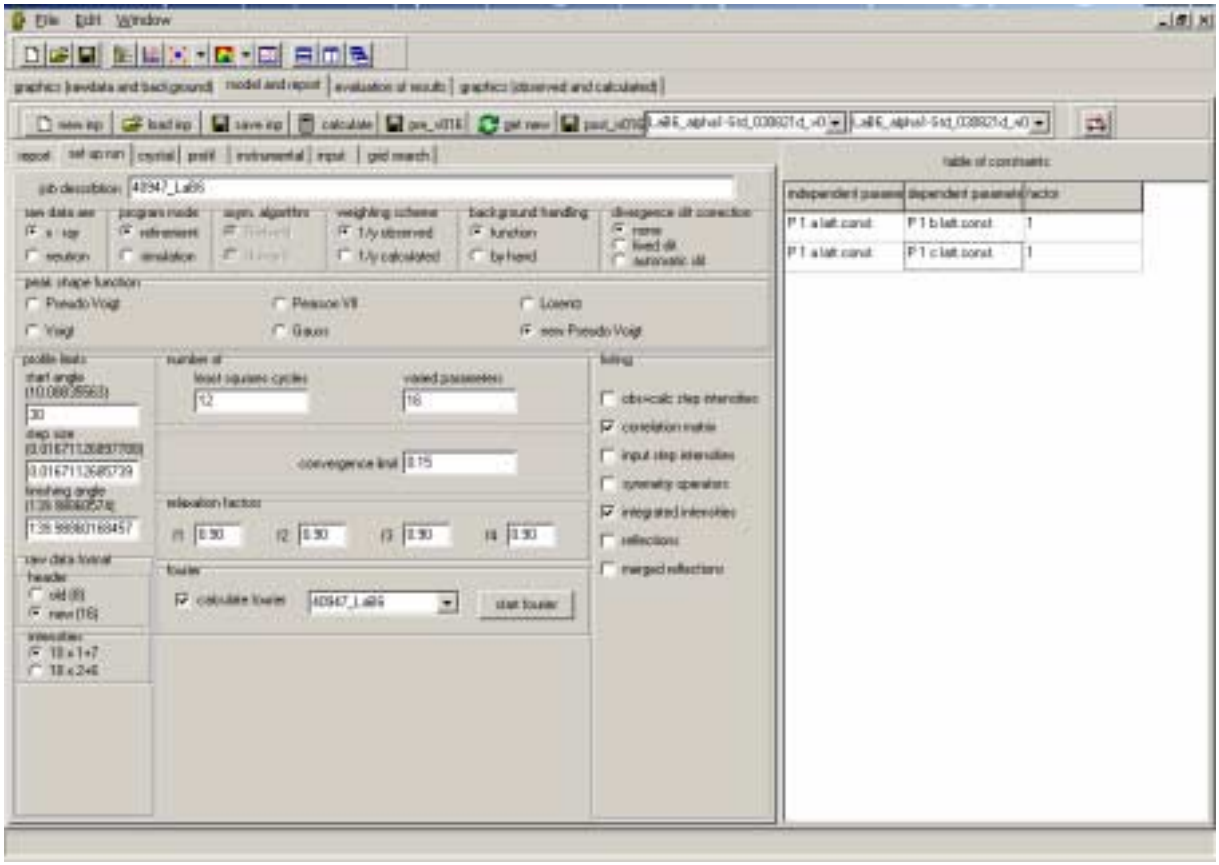


Fig. 4-1: The page *set up run* of the Rietveld window.

prepare a Rietveld run carefully modify or type in all necessary entries in the subpages *set up run* through *instrumental* of the main page *model and report*. If a Rietveld run fails this is usually due to invalid entries in one of these pages.

On the page *set up run* you usually have to check the type of *raw data*, the *program mode*, the *background handling*, the *divergence slit correction*, the *profile limits* to be taken into account for the refinement and the *number of least squares cycles*.

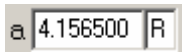
On the pages *crystal* and *profile* you can **define which parameters are to be refined**. Note that you can add a new phase by pushing *add phase*. In the following dialog you can choose a structure from a CIF file. To select a parameter for independent refinement just left click on the small field to the right of the respective entry. A flag "R" appears in the flag field, e.g. here  the lattice constant a has the current value 4.1565 and is flagged "R" to be refined independently during the next Rietveld run.

Fig. 4-2: The page *crystal* of the Rietveld window. Note that you can add a phase by hand or from a CIF file by pushing *add phase*.

If you wish to **set a hard constraint on a parameter** (i.e. to fix the "dependent" parameters' change by a factor to the change of an "independent" parameter) first drag and drop the independent parameter and then the dependent parameter to the *table of constraints*. For most parameters you are then asked to enter the factor which relates the changes of the dependent parameter to the changes of the independent parameter. This yields a "D" flag next to the dependent parameter and a new entry in the *table of constraints*. **To delete a constraint**

select the respective line in the *table of constraints* and then choose *delete selected row* from the context menu.

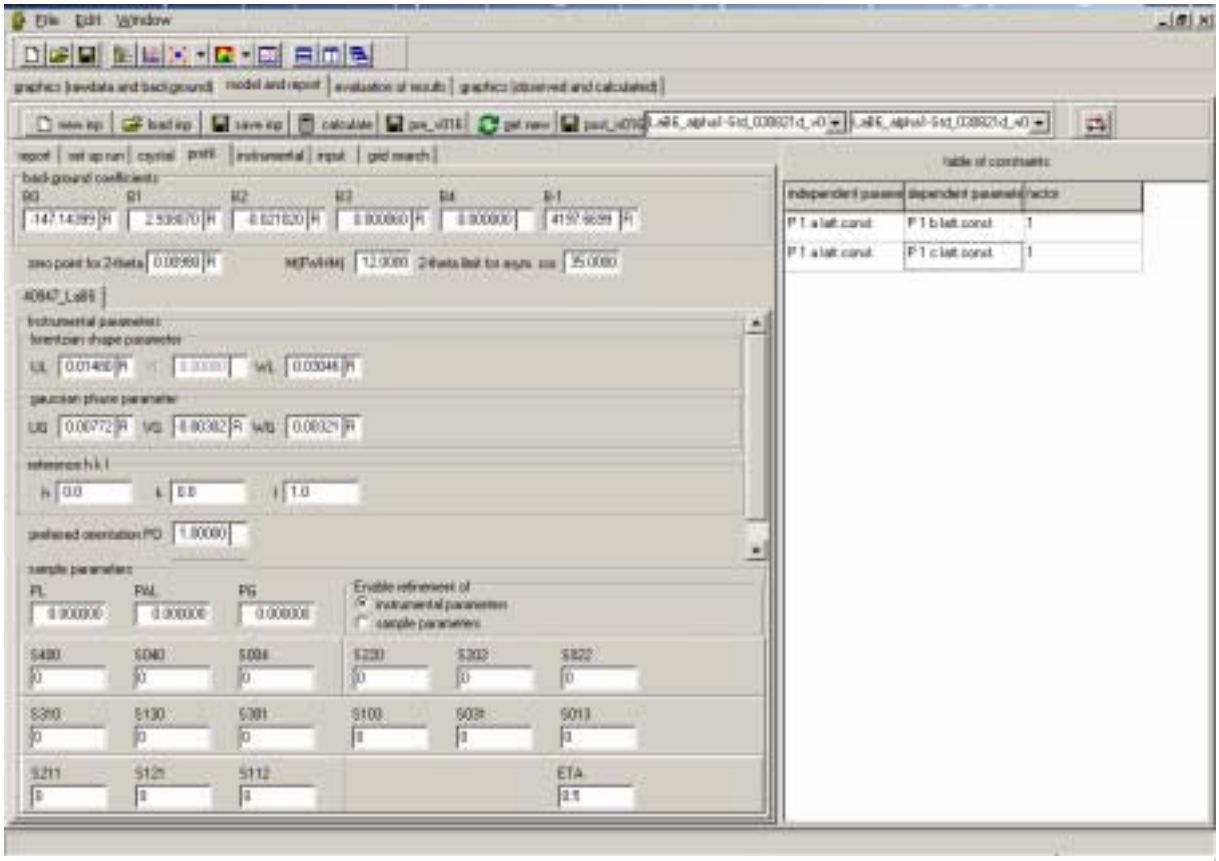


Fig. 4-3: The page *profile* of the Rietveld window.

On the page *profile* you find some global refineable or fixed parameters as well as the refineable profile parameters. Among the displayed parameters these things may not be self-evident:

- M(FWHM) is the "multiple of the full width at half maximum". It defines the range within which each single reflection is calculated as M(FWHM). Enlarging the value increases the computing time. A too low value will yield abruptly cut tails of the calculated reflections (to be checked in the graphics page) which may introduce aberrations to the calculated parameters.
- For a smooth background you will usually not need more than three or four of the background parameters. Use e.g. B_0, B_1, B_2 and B_3. Alternatively you can use the background handling by hand in which case you a) have to choose the appropriate option on the *set up run* page and b) have to set background points on the *graphics (rawdata…)* page.
- The "new Pseudo Voigt" function (see *set up run* page) is designed to separate the instrumental from the sample contributions to the observed reflection profiles. Since during a

refinement there is a strong correlation between some of the instrumental and the sample parameters you cannot refine parameters of these two groups at the same time. It is recommended to refine only the instrumental parameters for a profile-standard sample and use these as fixed input values for other samples which have been measured under the same conditions. For these only sample parameters should be refined. The calculation of strain and crystallite size values in the output file is based on this assumption.

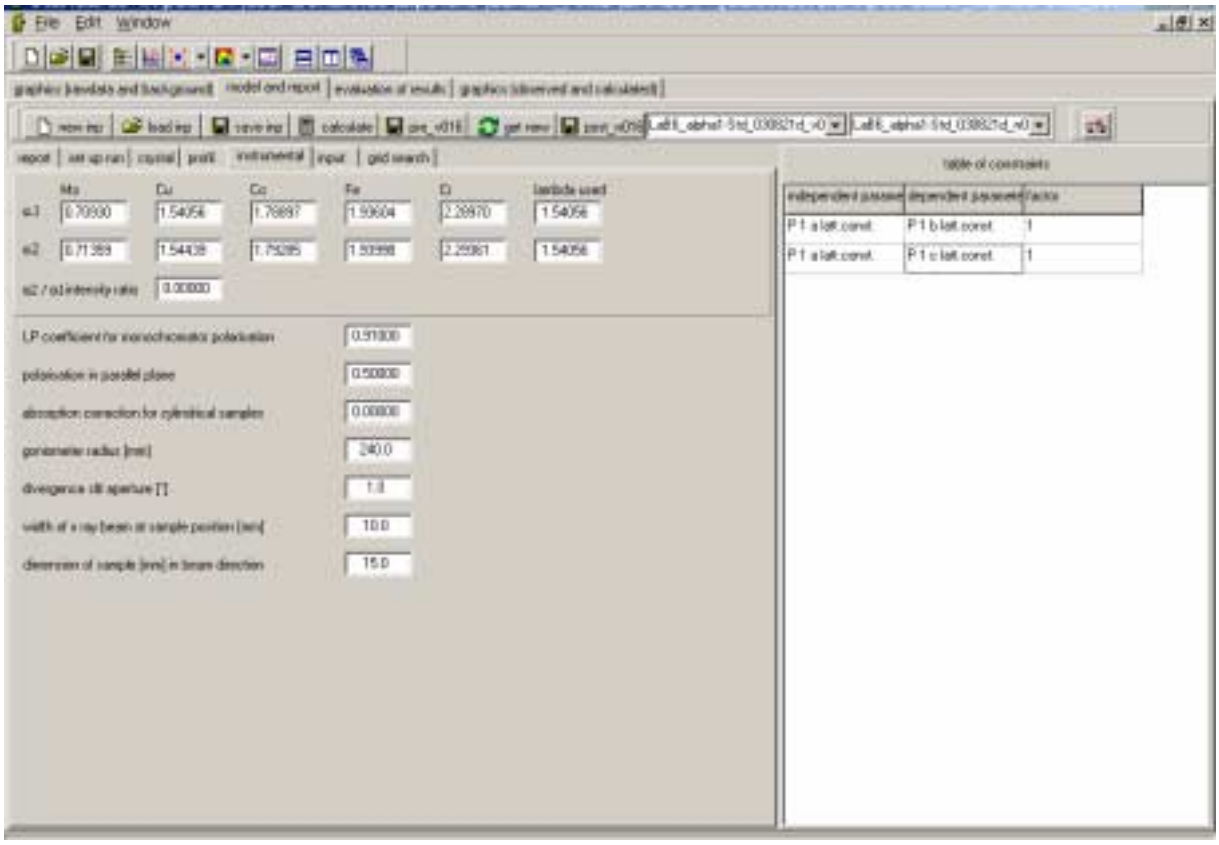
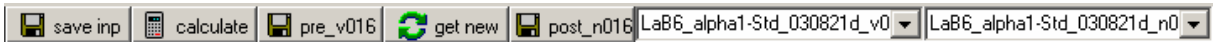


Fig. 4-4: The page *instrumental* of the Rietveld window.

On the page *instrumental* either select or type in the appropriate values. Note that some of these values are used for the calculation of correction factors due to over-irradiation of the sample (*goniometer radius*, *divergence slit aperture*, *width of...*, *dimension of...*) respectively absorption ($\mu \cdot R$ or $\mu \cdot d$, *goniometer radius*). μ·R is the product of the samples' linear absorption coefficient and the inner radius of the capillary, d is the thickness. The latter two only apply if transmission geometry was used, i.e. either with a capillary or a flat sample. The former one only applies for Bragg-Brentano geometry.

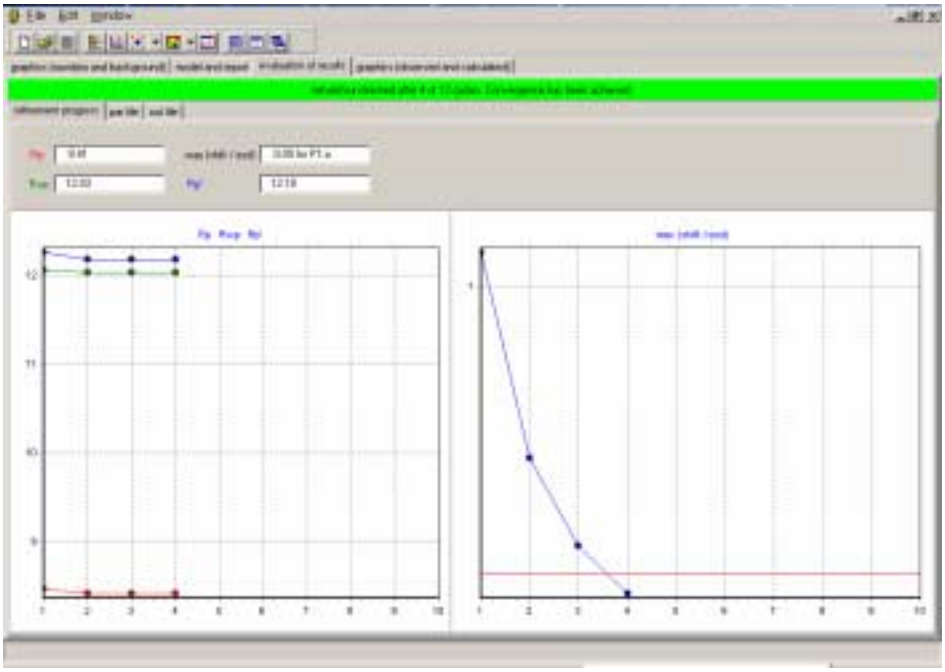
4.2.4 Performing a Rietveld run

The Rietveld job is controlled by the *Rietveld process bar*:

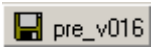


Experienced Rietveld users know well about the problem that after a bunch of refinement steps you may have run into some false minimum or the refinement diverges and you are possibly not able to restore your previous work. *BRASS* provides full user control to save versions of your input file at any time you wish and automatically records some information on certain user actions. In order to keep a clear track of the course of your refinement we recommend to follow the following procedure:

1. Type a comment on the next refinement step to the page *report*.
2. Apply any change to the input model that you need to prepare the next step.
3. Push [save inp] to save your changes to the current INP file.
4. Push [calculate] to run the Rietveld refinement. Now the program switches to the page *refinement progress* (see below) of the main page *evaluation of results*. Here you are informed about the progress of the last refinement step with respect to residuals ("R values") and convergence. If convergence has been achieved, i.e. *max(shift/esd)*, the largest ratio Δp/ESD(p) is lower than the user defined convergence criterion[2] (see *set up run* on page *model and report*), you are informed by a green bar. If convergence has not been achieved, but no fatal error occurred, then you are informed by a yellow bar. If a fatal error occurred during the Rietveld run you are informed by a red bar. In the latter case carefully check your input values and restart *BRASS*.



[2] Δp = Change of the parameter p in the last cycle of the current Rietveld run. ESD = estimated standard deviation, calculated from the diagonal elements of the inverted least squares matrix.

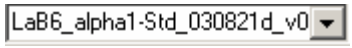
5. Check the results of the refinement for plausibility. (Use the pages *evaluation of results*, *graphics (observed and calculated)* and possibly *STRUPLO*).
6. If the refinement was successful push 

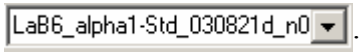
to save the status of the INP file as it was before the refinement, i.e. the "pre version". (Note that the version no. vXXX varies after each push).
7. If you wish to accept the changes from the refinement push

to overwrite the current INP file with the new values.
8. a) If the refinement has converged push

to save the updated version of your current INP file, i.e. the "post version". In addition the files OUT, PAR, PLT, PKS and NRF are saved with the same version number[3]. (Note that version nXXX varies after each push).
   b) If the refinement has not converged: Repeat steps 5 and 7 until convergence has been achieved and then push

.

The merits of this recommended procedure are: After the refinement you have a full report on every step of the refinement. More important: If the refinement crashes or you believe that you should follow a different strategy from a specific former step you can easily go back to this specific step and do so. Just select the respective version number from the list of "pre-versions" vXXX 

or from the list of "post-versions" nXXX 

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4.2.5 Displaying a structure model from the Rietveld input

While the *rietveld* window is open push the drop down button in the *project managing bar* in order to view a list of options for starting a *STRUPLO* job (e.g. see below). Alternatively on the page *crystal* (on main page *model and report*) push the button

to open *STRUPLO*.

Then follow the instructions in part 4.3 to display and manipulate the structure model of the chosen phase.

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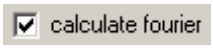
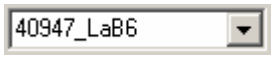
[3] OUT files provide the full report on all cycles of the last Rietveld run. PAR files contain the numerical values of refined parameters and some other quantities for all cycles of the last run. PLT files contain the resulting Rietveld plot. PKS files list the positions of all reflections of all phases. NRF files also contain all reflections but with additional information on each reflection.

4.2.6 Calculating and displaying Fourier maps

On the page *set up run* dialog of main page *model and report* check 

for routine preparation of the Fourier input file during a Rietveld refinement. Then select a phase from the drop-down list 

and push the button

to run the Fourier calculation. This invokes the opening of the Fourier window. Please follow the instructions of part 4.5 to learn about the use of the Fourier window.

4.2.7 Calculating and displaying a grid search

Not accomplished yet.

4.3 Running a STRUPLO 2003 job

4.3.1 Open or create a file.

To open a structure push . STRUPLO accepts three input data formats: (1) The new format within BRASS (file extension bst) written by the user interface, (2) The old STRUPLO format of the ascii input file (file extension str) and cif files. However, saving and exporting data is always in the internal bst format.

To create a new structure drawing choose the button .

4.3.2 General tool bars

Graphical items can be switched on and off using the tool bar (unit cell outlines, atoms, bonds, polyhedra, system of axes).

A B C D E F G H I

(A) Print current drawing (not working properly on some systems, use B instead)

(B) Export current drawing to a bitmap file. Enter resolution in the pop up edit menu

(C) Set attributes (see above)

(D) Search a certain position in the structure drawing

(E) Delete single items (atoms, bonds, polyhedra) by selecting the check box. Mouse click on the respective item will delete it and restore the background. Any deleted item can be restored from the item list.

(F) Calculate distances and angles

(G) Light source settings

(H) Identify any item on mouse click. The coordinates will be displayed in the lower right corner of the screen.

The drawing can be scaled, rotated, and shifted using the right hand side bars. The numbers 10, 1, and 0.1 define the steps [°] for rotating the drawing, or for shifting it. The other items are explained below. Press one of the ▲ arrows to perform the action with the selected steps.

shift drawing

rotate drawing

move cross (system of axes)

rotate about x or y (selected); shift up, down, left, right (selected)

rotate about z (selected); scale drawing (selected)

undo

redo

reset to initial setting

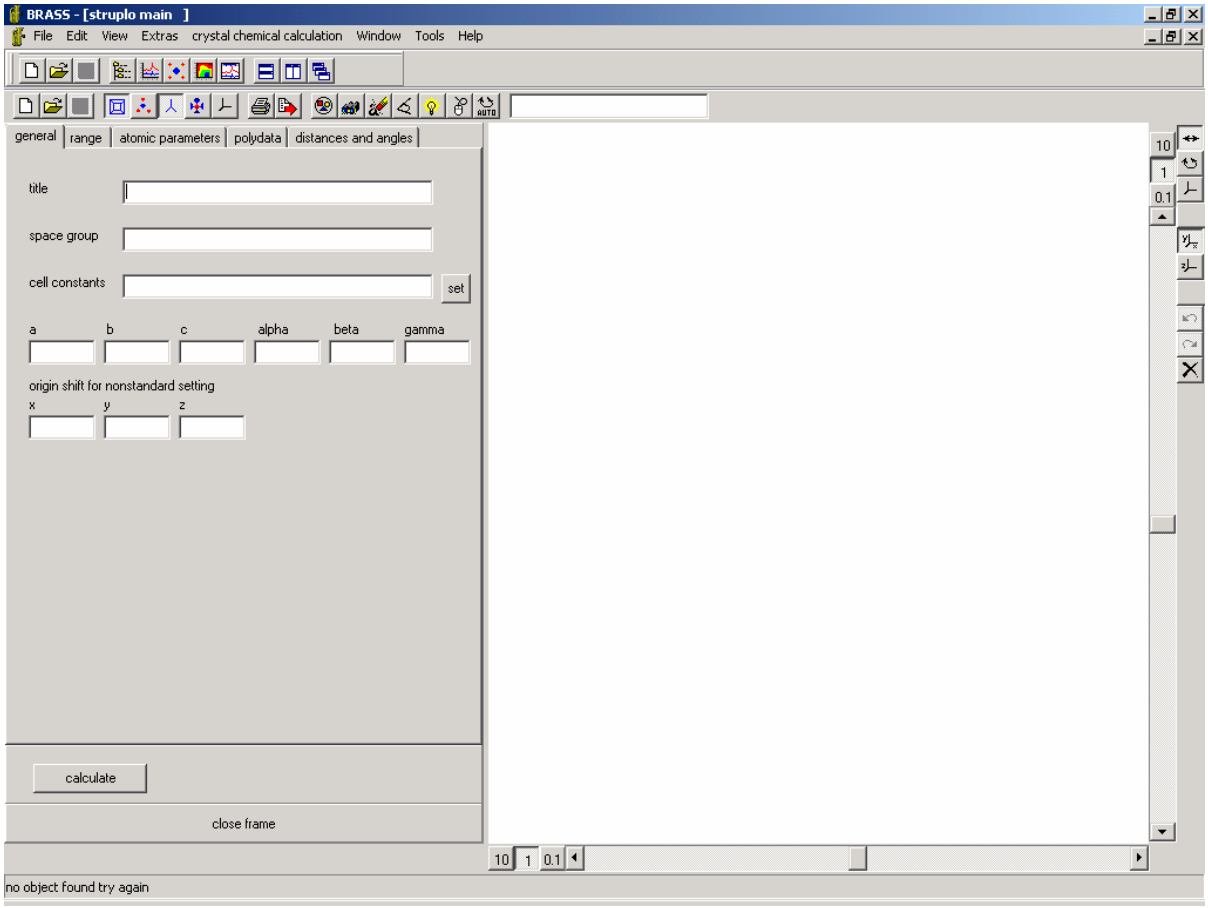
4.3.3 Pages with editing options

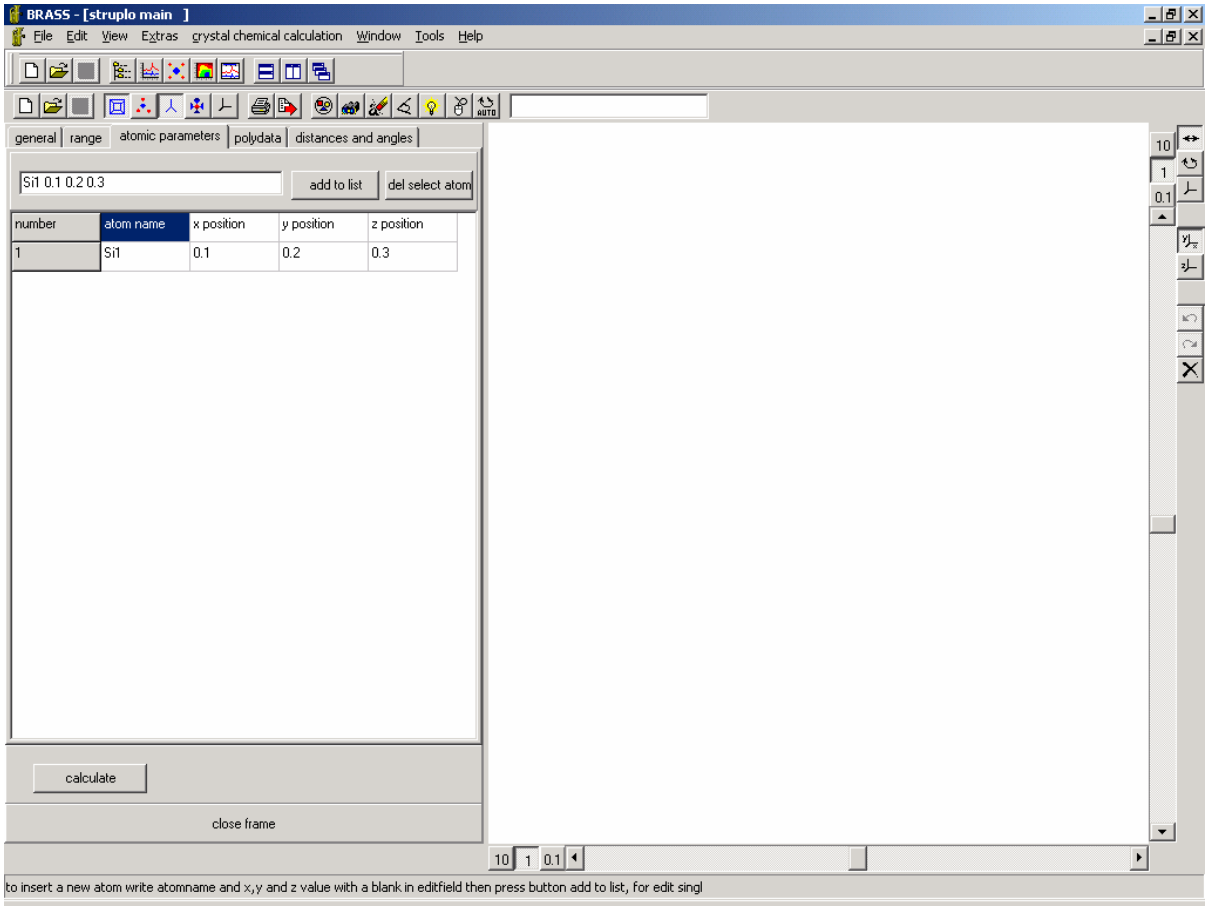
Creating a new file, i.e., creating a new structure drawing, as well as editing current data opens a set of overlapping pages with edit fields and input panels for the atomic data and drawing instructions which are described below.

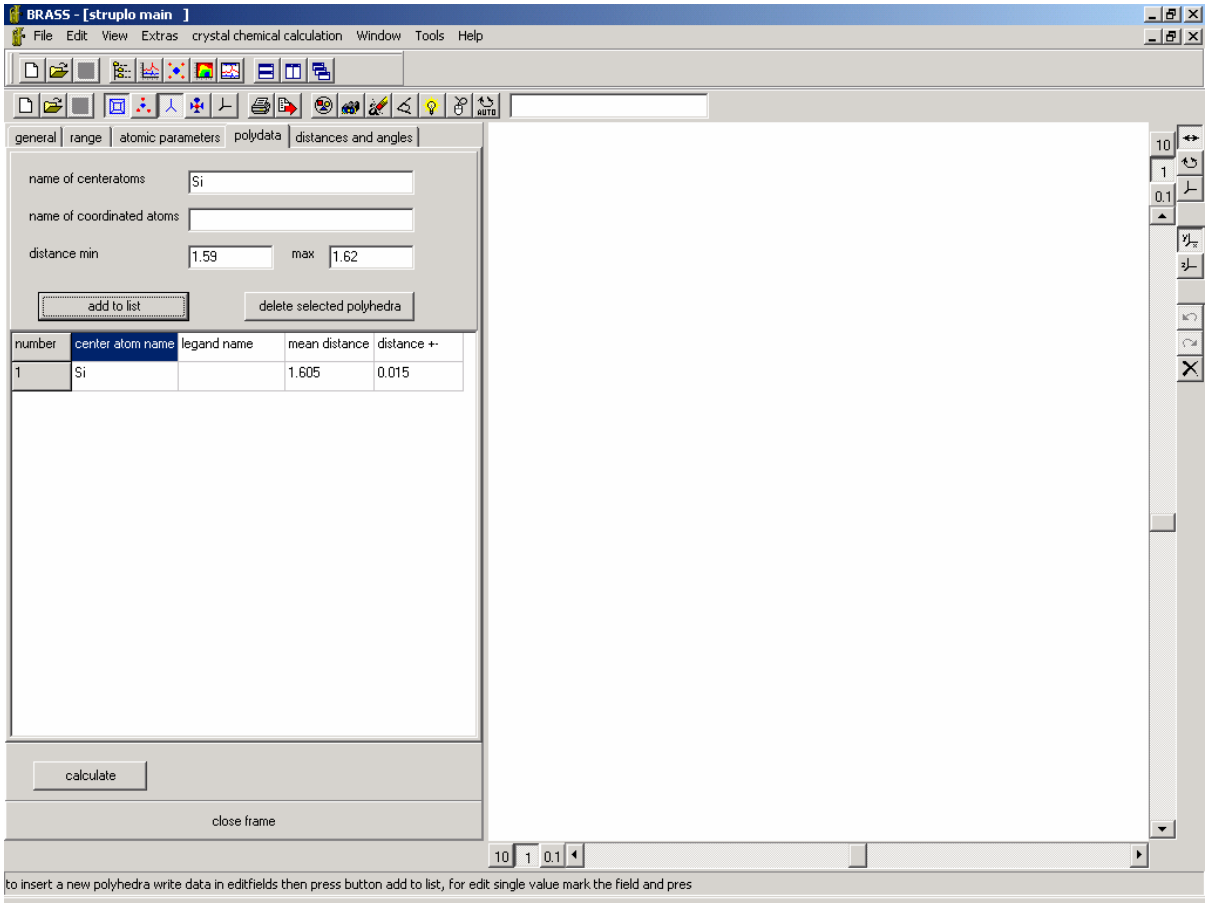
On the page *general* title, space group, and cell parameters are entered. Cell constants can be entered directly into the respective edit fields or they can be entered in one line separated by a space and then set by pushing the set button. Space group symbols are entered according to the syntax used in the old STRUPLO. Origins deviating from the standard setting in the International Tables can be chosen by entering an origin shift.

The page *range* defines the range of drawing given by the crystallographic coordinates as minimum and maximum values in *x*, *y*, and *z* direction.

Atom coordinates are entered on the page *atomic parameters*. Atom name, x, y, and z are entered in one line and then set by pressing “add to list”.


BRASS - [struplo main]
File Edit View Extras crystal chemical calculation Window Tools Help
general range atomic parameters polydata distances and angles
title
space group
cell constants
set
a b c alpha beta gamma
origin shift for nonstandard setting
x y z
calculate
close frame
no object found try again

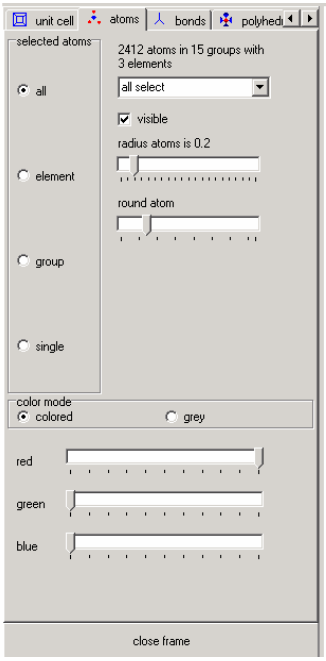

BRASS - [struplo main]
File Edit View Extras crystal chemical calculation Window Tools Help
general range atomic parameters polydata distances and angles
Si1 0.1 0.2 0.3
add to list
del select atom
number atom name x position y position z position
1 Si1 0.1 0.2 0.3
calculate
close frame
to insert a new atom write atomname and x,y and z value with a blank in editfield then press button add to list, for edit singl



Polyhedra are defined on the “polydata” page by entering the name of the central atom and the minimum and maximum distance to the ligands. The values are changed to the mean distance and the radius around the central atom representing a sphere in which coordinated atoms are drawn.

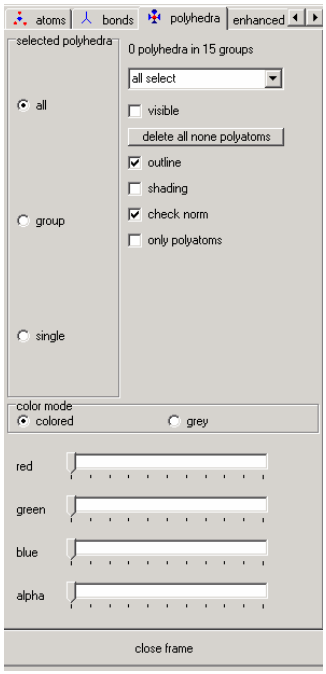
The crystal structure is displayed after pressing calculate .

All attributes are modified by selecting .



On this page atoms or groups of atoms are selected to be displayed. Attributes are assigned either to all atoms, to special elements (e.g. Si), to groups of atoms (e.g. Si 1) or to single atoms. To select the respective items press the pull down menu on top. Radius is given in Å, the degree of rounding atoms (the number of line segments used to draw a circle) is set by the scrollbar. Color or grey scale mode is selected by the two radio buttons. If color mode is selected the colors are set by the three scroll bars.

Bonds are defined by entering the minimum and maximum values for the interatomic distances between neighboring atoms. Color and size can be selected using the scrollbars.

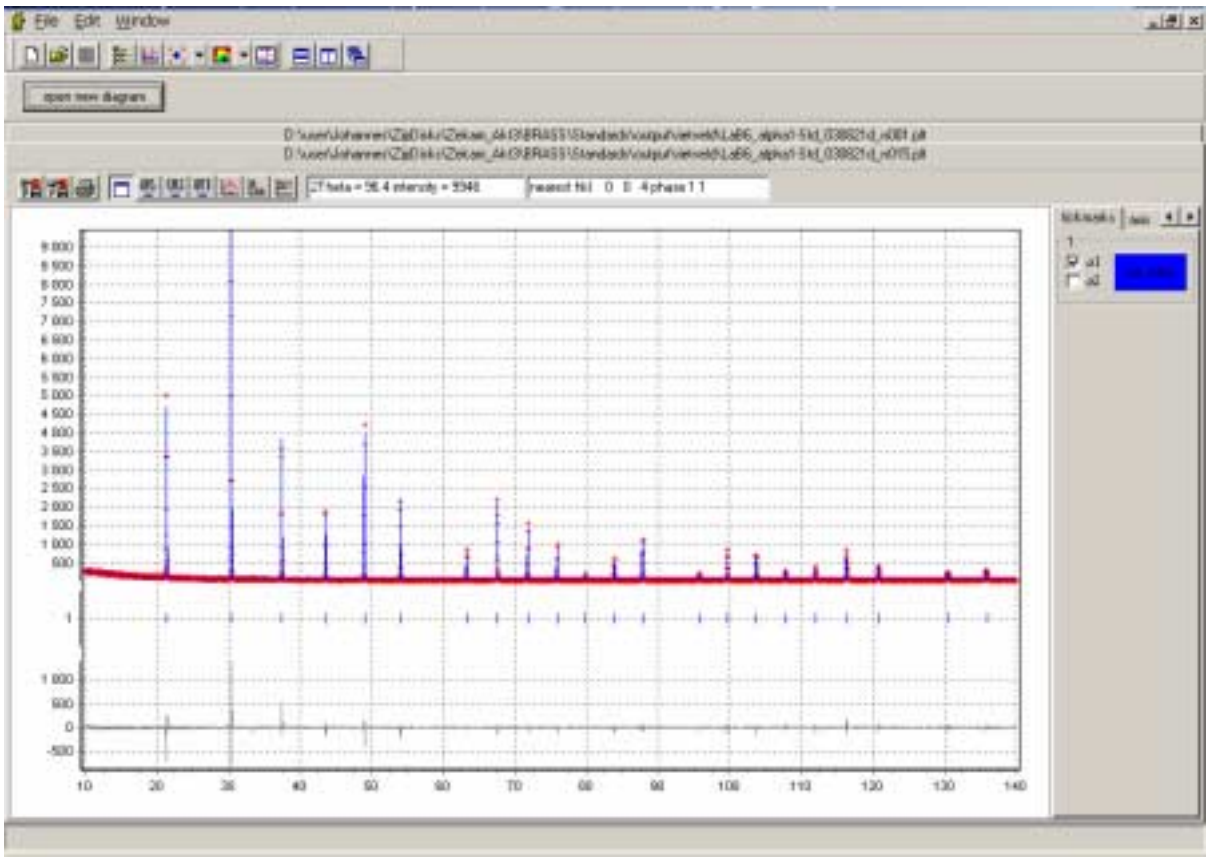


The attributes for polyhedra can be selected for all polyhedra, for groups, or for single polyhedra as described for the atom settings. All atoms drawn as spheres but not belonging to a polyhrdron can be deleted by pressing . The check boxes define the further layout. The page “enhanced” must be used to define the outline settings.

Description of the other options will be added soon.

4.4 Using the Rietveld plot Viewer

The *Rietveld plot viewer* is used to display Rietveld PLT files which are stored in your file system without having to run a current Rietveld job in advance. You can open up to (Akt hier weiter: Thomas fragen, wieviele!) diagrams e.g. in order to evaluate the quality of the refinement obtained after different steps:



4.5 Displaying stored Fourier maps

In the *Fourier* window you can

- Display an existing Fourier maps when opening a *.BFO file.
- Display a freshly calculated Fourier map called from the *Rietveld* window (page *set up run* of main page *model and report*, see 4.2.6).
- Perform and display the results of a fourier calculation. Note that the fourier calculation is always based on the current file riet.fou.

On the page *cell data* you see the basic input for the calculated map (see fig. below).

On the pages *difference diagram*, *based on F_C diagram* and *based on F_O diagram* the respective Fourier plots are displayed (see fig. below). You have a number of options to ma-

nipulate the type and the appearance of the plots by the *Fourier tool bar* and the settings on page *set levels*. On the right hand side note the list of sections that have been calculated and that can be flicked through in a very fast manner.